PHOTODISSOCIATION DYNAMICS OF A TRIATOMIC PSEUDO-DIHALIDE: ABSORPTION CROSS SECTION AND DYNAMICS OF SOLVATED ICN^-

JOSHUA P. MARTIN, QUANLI GU[a], JOSHUA P. DARR[b], *JILA, Department of Chemistry and Biochemistry University of Colorado at Boulder, Boulder, CO 80309*; ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*; and W. CARL LINEBERGER, *JILA, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309*.

We report the photoabsorption cross section and photoproduct branching ratios of mass-selected bare ICN^- and $ICN^-(CO_2)$ following excitation to the $A'\ ^2\Pi_{1/2}$ electronic excited state. Previous studies of CO_2 solvated-heteronuclear dihalides, $IX^-(CO_2)_n$ (X=Cl, Br), reported three excited state selective classes of photoproducts: I^-, X^-, and IX^- based clusters. Photoabsorption of bare ICl^- and IBr^- that leads to population in the $A'\ ^2\Pi_{1/2}$ state have maxima near 680 nm and 740 nm, respectively, and result in I^- photoproducts exclusively over the entire band corresponding to $A'\ ^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}$ excitation. Interestingly, following excitation of bare ICN^- to the comparable state (430-650 nm, maximum at 490 nm), I^- is the dominant ionic photoproduct, but CN^- photoproducts are observed as well. When a single CO_2 solvent molecule is added to ICN^-, the same $A'\ ^2\Pi_{1/2} \leftarrow X^2\Sigma_{1/2}$ excitation results in apparent charge transfer within the complex. Therefore, the observed ionic photoproducts are not just the expected I^- and $I^-(CO_2)$, but CN^- and solvated $CN^-(CO_2)$ photoproducts are also significant products. Analysis of the experimental results using calculated potential energy curves of ICN^- reveals intriguing dynamics of the photoexcited triatomic pseudo-dihalide. Supported by NSF and AFOSR.

[a]Present address: Department of Chemistry, University of Virginia, Charlottesville, VA 22904
[b]Present address: Department of Chemistry, University of Nebraska, Omaha, NE 68182